

Molecular devices*

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Abstract: The concept of a macroscopic device can be extended to the molecular level by designing and synthesizing (supra)molecular species capable of performing specific functions. Molecular devices need energy to operate and signals to communicate with the operator. The energy needed to make a device work can be supplied as chemical energy, electrical energy, or light. Luminescence is one of the most useful techniques to monitor the operation of molecular-level devices. The extension of the concept of a device to the molecular level is of interest, not only for basic research, but also for the growth of nanoscience and the development of nanotechnology. In this article, some of the most recent experiments performed in our laboratory will be reviewed.

INTRODUCTION

The progress of civilization has always been related to the construction of novel devices. In the last 50 years, progressive miniaturization of the components employed for the construction of devices has resulted in outstanding achievements, particularly in the field of information technology.

The miniaturization of components for the construction of useful devices is currently pursued by the top-down approach. This approach, which is in the hands of physicists and engineers, consists in manipulating progressively smaller pieces of matter by photolithography and related techniques. It is becoming clear, however, that the top-down approach is subjected to drastic limitations for dimensions smaller than 100 nm [1].

An alternative strategy toward technology at the nanometer scale is offered by the bottom-up approach, which starts from molecules and builds up to nanostructures. Chemists, by the nature of their discipline, are already at the bottom, since they are able to manipulate molecules, the smallest entities of matter with distinct shapes and properties. Chemists are, therefore, in an ideal position to develop bottom-up strategies for the construction of nanoscale devices. In fact, the molecule-by-molecule bottom-up strategy is nothing else than supramolecular chemistry, a discipline which emerged in the late 1970s and which has been extensively developed in recent years [2].

DEVICES FOR PHOTOINDUCED ENERGY OR ELECTRON TRANSFER

Photoinduced energy and electron transfer are basic processes for connecting light energy inputs with a variety of optical, electrical, and mechanical functions. Several devices can be designed for delivering electronic energy or electrons, in a controlled way, to predetermined components in a supramolecular system. For space reasons, wires (see, e.g., ref. [3]) and switches (see, e.g., ref. [4]) will not be described.

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Molecular plug/socket

Supramolecular species whose components are connected by means of noncovalent forces can be disassembled and reassembled [5] by modulating the interactions that keep the components together, thereby allowing switching of electron- or energy-transfer processes. Two-component systems of this type are reminiscent of plug/socket electrical devices and, like their macroscopic counterparts, must be characterized by (i) the possibility of connecting/disconnecting the two components in a reversible way, and (ii) the occurrence of an electron or electronic energy flow from the socket to the plug when the two components are connected (Fig. 1a). Hydrogen-bonding interactions between ammonium ions and crown ethers are particularly convenient for constructing molecular-level plug/socket devices since they

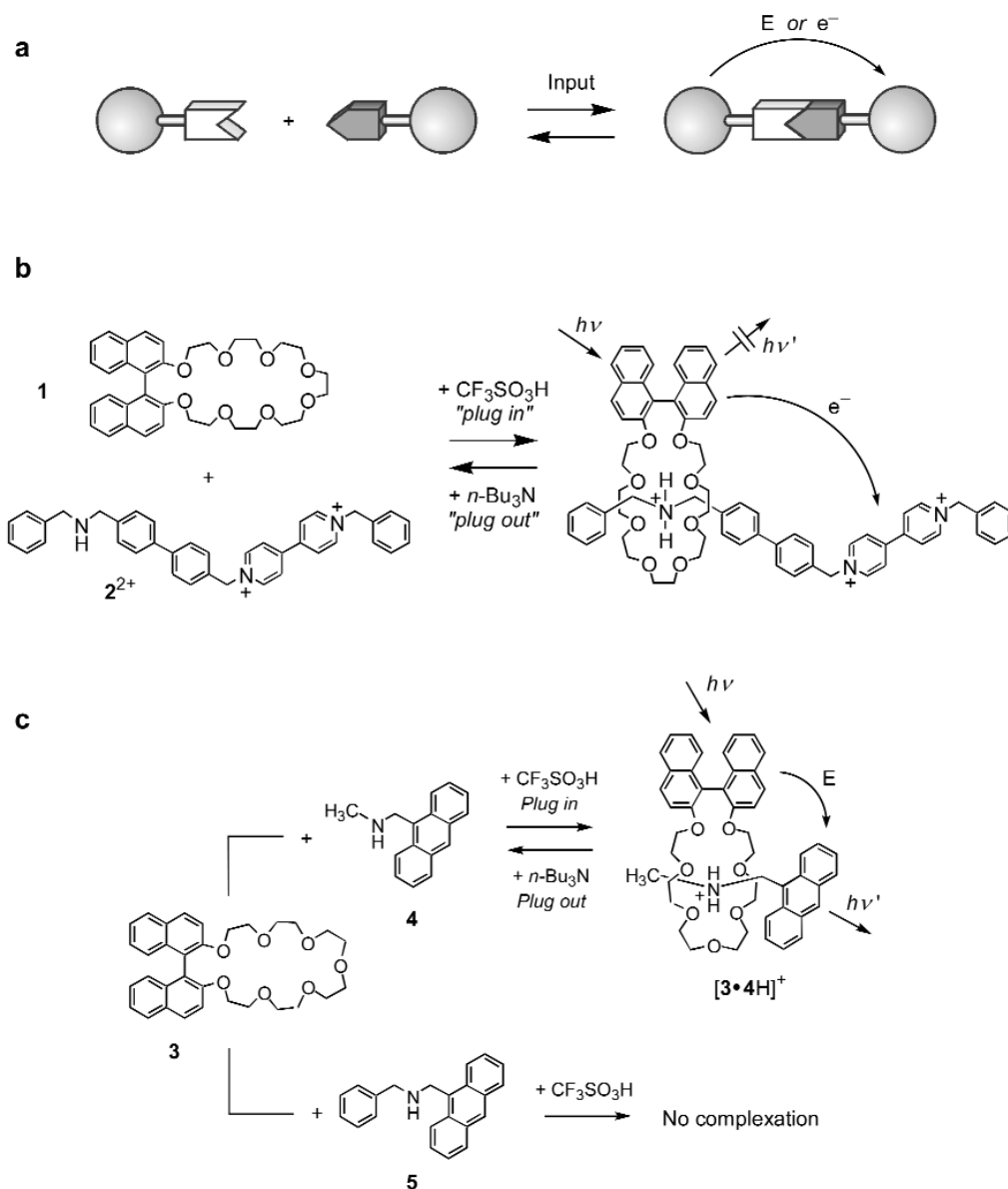


Fig. 1 Schematic representation of a plug/socket system (a); switching of photoinduced electron [6] (b) and energy [7] (c) transfer by acid/base controlled plug in/plug out of suitable molecular components.

can be switched on and off quickly and reversibly by means of acid/base inputs. In the system illustrated in Fig. 1b, the plug-in function is related to the threading, driven by formation of strong $[N^+ \cdots H \cdots O]$ hydrogen bonds in nonpolar solvents, of (\pm)-binaphthocrown ether **1** by the dialkylammonium moiety of the wire-like compound $[2H]^{3+}$, obtained by protonation of amine 2^{2+} [6]. In the plugged-in pseudorotaxane structure, an electron-transfer process to the bipyridinium unit of $[2H]^{3+}$ takes place upon light excitation of the binaphthyl unit of the macrocycle, causing quenching of the typical binaphthyl fluorescence. Addition of a stoichiometric amount of base, which deprotonates the ammonium ion, causes the recovery of the binaphthyl fluorescence, demonstrating that plug-out of the pseudorotaxane structure has occurred.

A similar plug/socket system, which deals with the transfer of electronic energy, is illustrated in Fig. 1c [7]. The absorption and fluorescence spectra of a CH_2Cl_2 solution containing equal amounts of (\pm)-binaphthocrown ether **3** and amine **4** indicate the absence of any interaction between the two compounds. Addition of a stoichiometric amount of acid causes profound changes in the fluorescence behavior of the solution, namely (i) the fluorescence of **3** is quenched, and (ii) the fluorescence of $[4H]^+$ is sensitized upon excitation with light absorbed exclusively by the crown ether. These observations are consistent with the formation of a pseudorotaxane-type adduct wherein very efficient energy transfer takes place from the binaphthyl unit of the crown ether to the anthracenyl group incorporated within the dialkylammonium ion. Such a pseudorotaxane can be disassembled by the subsequent addition of a stoichiometric amount of base, thereby interrupting the photoinduced energy flow, as indicated by the fact that the initial absorption and fluorescence spectra are restored. Interestingly, the plug-in process does not take place when a plug component incompatible with the size of the socket, such as the benzyl-substituted amine **5**, is employed (Fig. 1c).

Molecular extension cable

The plug/socket concept can be used to design molecular systems which mimic the function played by a macroscopic electrical extension cable. An extension cable is more complex than a plug/socket device since there are *three* components held together by *two* connections that have to be controllable *reversibly* and *independently*; in the fully connected system, an electron or energy flow must take place between the remote donor and acceptor units (Fig. 2a).

In the attempt to construct a molecular-level extension cable, the [3]pseudorotaxane shown in Fig. 2b, made of the three components 6^{2+} , $[2H]^{3+}$, and **7**, has been recently synthesized and studied [6]. Component 6^{2+} consists of two moieties: a $[Ru(bpy)_3]^{2+}$ unit, which plays the role of electron donor under light excitation, and a crown ether, which plays the role of a first socket. The ammonium center of $[2H]^{3+}$, driven by hydrogen-bonding interactions, threads as a plug into the first socket, whereas the bipyridinium unit, owing to charge-transfer (CT) interactions, threads as a plug into the third component, **7**, which plays the role of a second socket. In CH_2Cl_2/CH_3CN (98:2 v/v) solution, reversible connection/disconnection of the two plug/socket functions can be controlled independently by acid/base and red/ox stimulation, respectively. In the fully connected triad, light excitation of the $[Ru(bpy)_3]^{2+}$ unit of component 6^{2+} is followed by electron transfer to the bipyridinium unit of component $[2H]^{3+}$, which is plugged into component **7**. Although the transferred electron does not reach the final component of the assembly, the intercomponent connections employed fulfil an important requirement, namely, they can be controlled reversibly and independently. Possible schemes to improve the system have also been discussed [6].

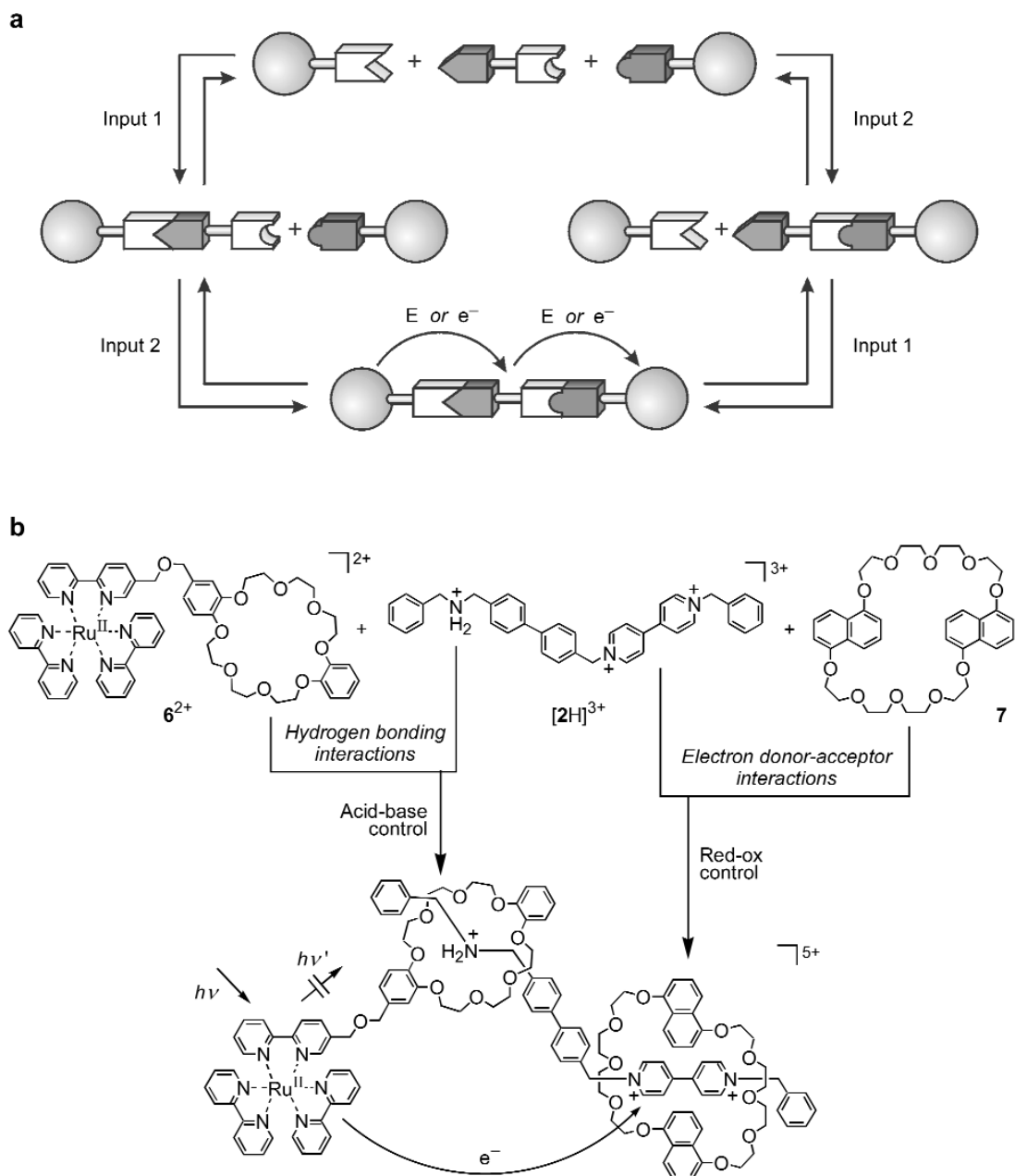


Fig. 2 Schematic representation of an extension cable (a); a supramolecular system that behaves as a molecular-level extension cable (b) [6].

Dendrimers as antenna systems

In suitably designed dendrimers, electronic energy transfer can be channeled toward a specific position of the array. Compounds of this kind play the role of antennas for light harvesting. Several light-harvesting dendrimers have been recently investigated [8]. Some examples are illustrated below.

A dendrimer with a metal complex as a core

In the dendritic complex shown in Fig. 3, the 2,2'-bipyridine ligands of the $[\text{Ru}(\text{bpy})_3]^{2+}$ -type core carry branches containing 1,3-dimethoxybenzene- and 2-naphthyl-type chromophoric units [9]. Since such units (as well as the core) are separated by aliphatic connections, the interchromophoric interactions are weak and the absorption spectra of the dendrimer is substantially equal to the sum of the spectra of the chromophoric groups that are present in its structures. The three types of chromophoric groups, namely, $[\text{Ru}(\text{bpy})_3]^{2+}$, dimethoxybenzene, and naphthalene, are potentially luminescent species. In the dendrimer, however, the fluorescence of the dimethoxybenzene- and naphthyl-type units is almost completely quenched in acetonitrile solution, with concomitant sensitization of the luminescence of the $[\text{Ru}(\text{bpy})_3]^{2+}$ core ($\lambda_{\text{max}} = 610 \text{ nm}$). These results show that a very efficient energy-transfer process takes place converting the very short-lived UV fluorescence of the aromatic units of the wedges to the long-lived orange emission of the metal-based dendritic core. It should also be noted that in aerated solution the luminescence intensity of the dendrimer core is more than twice intense as that of the $[\text{Ru}(\text{bpy})_3]^{2+}$ parent compound because the dendrimer branches protect the Ru-bpy based core from dioxygen quenching [9]. In conclusion, because of the very high absorbance of the naphthyl groups in the UV spectral region, the high energy-transfer efficiency, and the strong emission of the $[\text{Ru}(\text{bpy})_3]^{2+}$ -type core, dendrimer 6^{2+} (Fig. 3) exhibits a strong visible emission upon UV excitation even in very dilute ($10^{-7} \text{ mol l}^{-1}$) solutions.

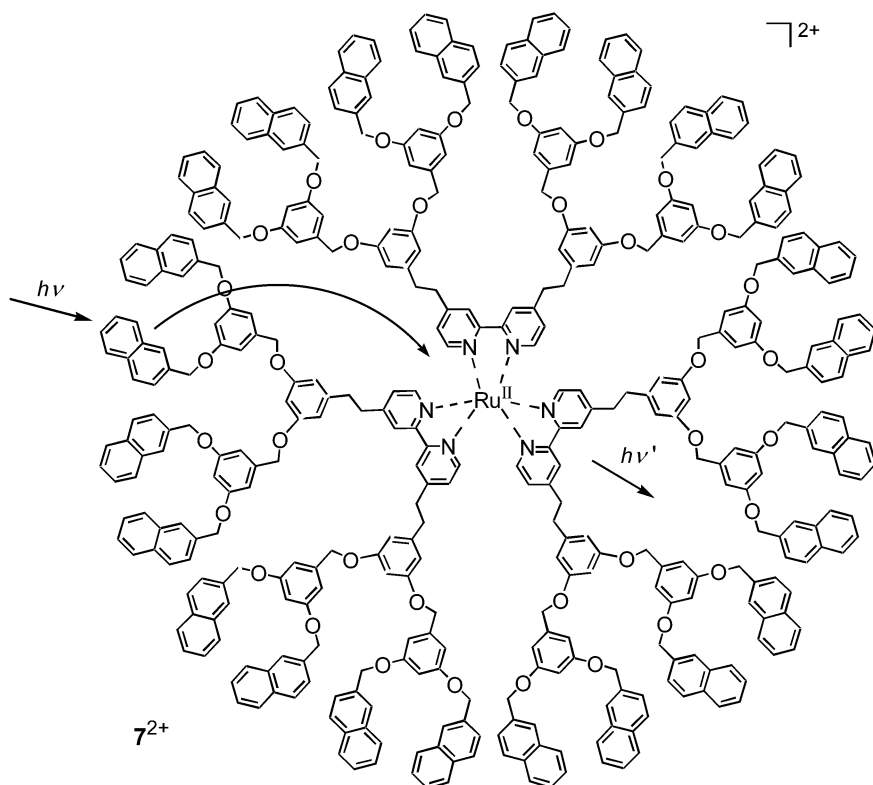


Fig. 3 Antenna effect in a dendrimer [9].

Host/guest dendrimer-based systems

An important property of dendrimers is the presence of internal cavities where ions or neutral molecules can be hosted [10,11]. Such a property can potentially be exploited for a variety of purposes, which in-

clude catalysis and drug delivery. Energy transfer from the numerous chromophoric units of a suitable dendrimer to an appropriate guest may result in a light-harvesting antenna system. An advantage shown by such host/guest light-harvesting systems is that the wavelength of the resulting sensitized emission can be tuned by using the same dendrimer and different types of guests.

The dendrimer shown in Fig. 4 consists of a hexamine core surrounded by 8 dansyl-, 24 dimethoxybenzene-, and 32 naphthalene-type units [12]. In dichloromethane solution, this dendrimer exhibits the characteristic absorption bands of the component units and a strong dansyl-type fluorescence. Energy transfer from the peripheral dimethoxybenzene and naphthalene units to the fluorescent dansyl units occurs with >90 % efficiency. When the dendrimer hosts a molecule of the fluorescent eosin dye (Fig. 4), the dansyl fluorescence, in its turn, is quenched and sensitization of the fluorescence of the eosin guest can be observed. Quantitative measurements show that the encapsulated eosin molecule collects electronic energy from all the 64 chromophoric units of the dendrimer with an efficiency >80 %

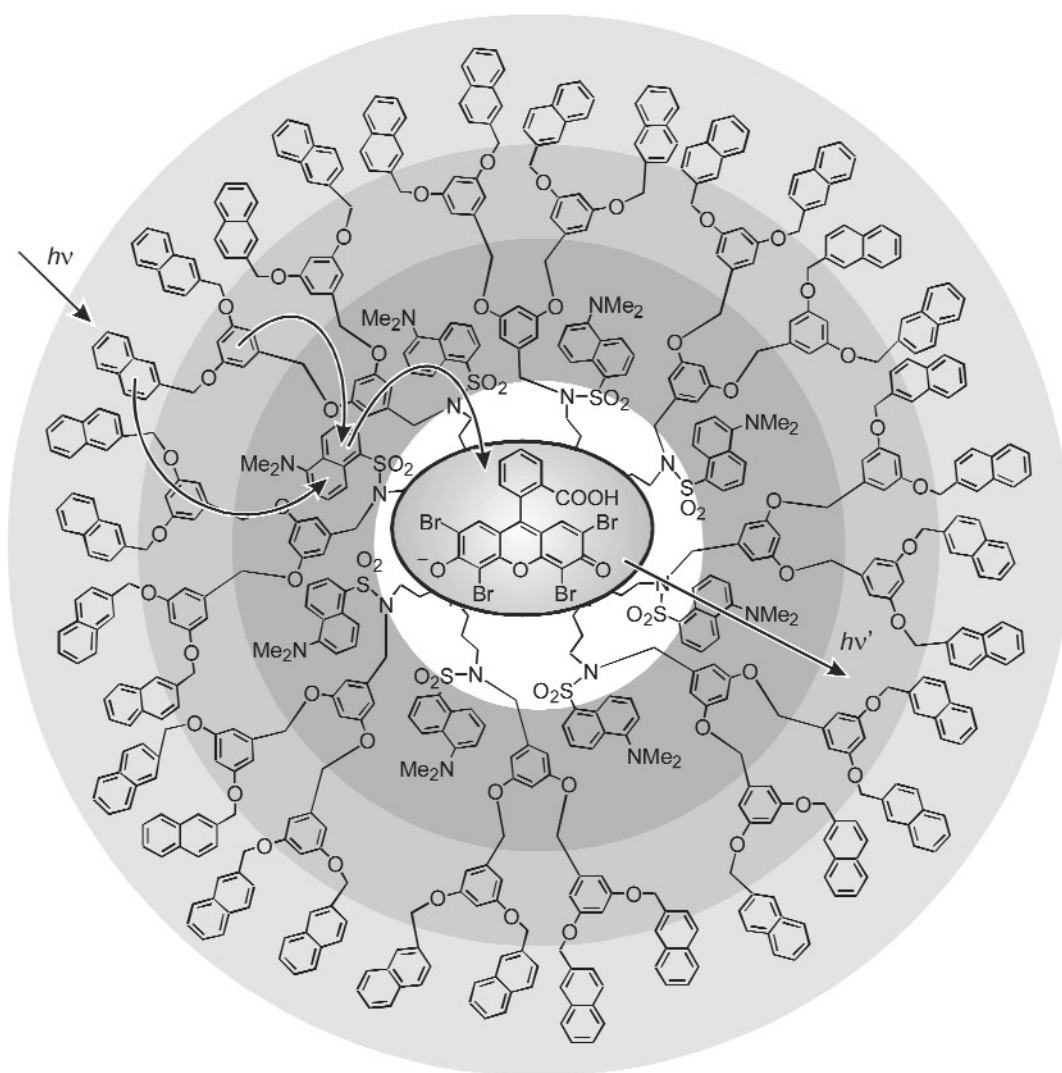


Fig. 4 Schematic representation of the energy-transfer processes taking place in a dendrimer which contains three different types of light-harvesting chromophoric units and a hosted eosin molecule [12].

(partial overlapping between dansyl and eosin emissions precludes a better precision). Both intramolecular (i.e., within dendrimer) and intermolecular (i.e., dendrimer host→eosin guest) energy-transfer processes occur very efficiently by a Förster-type mechanism because of the strong overlap between the emission and absorption spectra of the relevant donor/acceptor units. Lanthanide ions have also been incorporated into dendrimers containing dyes and amide units. In the case of Nd^{3+} , sensitization of the near-infrared emission (1064 nm) of the lanthanide ion has been obtained [13].

DEVICES FOR PHOTON-BASED INFORMATION PROCESSING

Logic gates

In present computer networks, data processing and communication require the encoding of information in electrical and optical signals in the form of binary digits. The logic circuits of microprocessor systems elaborate binary data through sequences of logic gates. Although it is not necessarily the case that the components of a molecular computer [14] will have to operate in ways analogous to those of conventional silicon-based computers, a great deal of effort has been devoted to the design, synthesis, and characterization of molecular systems in which silicon-based logic can, in principle, be mimicked. Indeed, molecular-level logic functions of several types as well as very interesting molecular-based combinational logic circuits have been reported and discussed in the last few years [15–18].

Molecular switches convert input stimulation into output signals. Therefore, the principles of binary logic can be applied to the signal transduction operated by these systems. In the molecular-level switches, stimulation is usually performed by optical, electrical, or chemical inputs and the produced outputs are again optical, electrical, or chemical. It should be pointed out that input/output molecular-level processes are very common, but their logic aspects have been recognized only recently [19]. As mentioned above, any kind of input/output signals can be used, but most of the described examples are based on fluorescence switching caused by photoinduced electron-transfer (PET) processes, as schematically illustrated in Fig. 5 [20]. In this figure, F is a potentially fluorescent unit (e.g., an anthracene molecule), whose fluorescent excited state is quenched by PET from the HOMO orbital of an appended electron-donor receptor, D (e.g., an amine unit). When the HOMO orbital of the electron donor is engaged by a suitable added molecule or ion (in the case of an amine, e.g., by protonation), fluorescence can be observed because the HOMO of the donor is lowered in energy and electron transfer can no longer occur. Fluorescence is an ideal output because of its ease of detection even at the single-molecule limit [21]. Another remarkable feature of fluorescent signals is that they do not need to be wired to operate. Light can indeed bridge the gap between the world of molecules and our macroscopic world.

For the sake of space, we will only illustrate two examples of molecular-level logic gates based on luminescence signal. An exhaustive discussion is given in Chapter 9 of ref. [22].

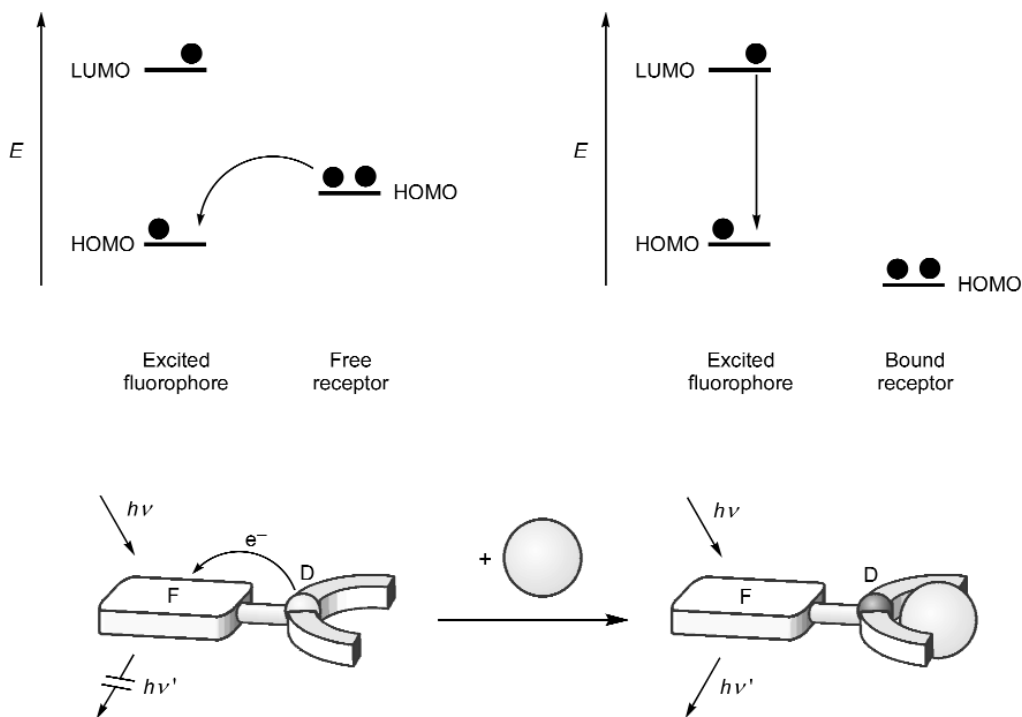


Fig. 5 Schematic illustration of fluorescence switching by photoinduced electron transfer (PET).

AND gate

The AND operator has two inputs and one output (Fig. 6a), and in a simple electrical scheme it can be represented by two switches in series. The best examples of molecular level AND gates are those based on two chemical inputs and an optical (fluorescence) output, but examples of molecular systems able to process chemical and optical inputs or two optical inputs with AND functions are also known [16]. Figure 6b illustrates the case of an anthracene derivative that produces a virtually perfect truth table [23]. In methanol, the fluorescence quantum yield in the presence of 10^{-3} mol l $^{-1}$ H $^{+}$ and 10^{-2} mol l $^{-1}$ Na $^{+}$ is 0.22 (output state 1, fourth line of the truth table, Fig. 6c), whereas none of the three output states

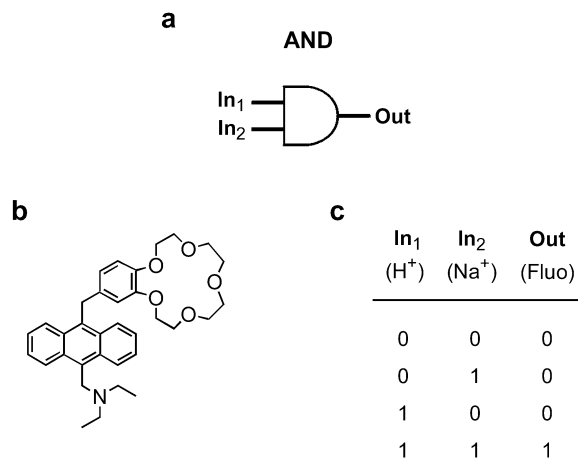


Fig. 6 Symbolic representation (a), molecular implementation (b), and truth table (c) of an AND logic gate based on a three-component system [23].

0 has quantum yield higher than 0.009. The PET quenching process involves the amine moiety in the first two states of the truth table and, of course, the crown ether in the third one. Interestingly, the crown ether alone would not be able to quench the anthracene fluorescence, but when the amine is protonated the process becomes thermodynamically allowed and it does occur.

XOR logic gate

The eXclusive OR (XOR) logic gate is particularly important because it can compare the digital state of two signals. If they are different an output 1 is given, whereas if they are the same the output is 0. This logic operation has proven to be difficult to emulate at the molecular scale, but some examples are now available [24,25].

The first reported molecular-level XOR gate is illustrated in Figs. 7 and 8 [24]. The electron-rich macrocycle **8** can be threaded by an electron-deficient wire-type molecule like **9**²⁺. The resulting pseudorotaxane [**8**·**9**]²⁺ is held together by CT interactions. Assembling is signalled by as many as three different optical channels: (i) appearance of a red color because of the presence of a CT absorption band in the visible region; (ii) disappearance of the blue-green fluorescence of **9**²⁺, and (iii) disappearance of the UV fluorescence of **8** with $\lambda_{\text{max}} = 343 \text{ nm}$ (the disappearance of the two fluorescent signals is due to the presence of the lower-lying CT state in the assembled system). For the XOR function, protons and *n*-Bu₃N are the inputs and the fluorescence of **8** at 343 nm is the output. The working mechanism of this system is illustrated schematically in Fig. 8 [24]. As mentioned above, in the absence of the two inputs the fluorescence of **8** is quenched in the pseudorotaxane (output 0). When the Bu₃N input alone is applied, the pseudorotaxane dethreads because of the formation of a stronger CT interaction between the amine and **9**²⁺. Under such conditions, **8** is free and its fluorescence is not quenched (amine input 1, output 1). Application of the H⁺ input causes protonation of **8** and, again, dethreading of the pseudorotaxane. Since protonation of **8** (presumably at the aliphatic ether oxygens) does not perturb its emission compared to the neutral form, the H⁺ input 1 causes an output 1. Therefore, the output achieves logic state 1 in the two situations in which *exclusively* one of the two inputs is present. However, when both inputs are applied in stoichiometric amounts, acid/base neutralization results, the pseudorotaxane remains intact and the 343 nm emission is quenched (output 0).

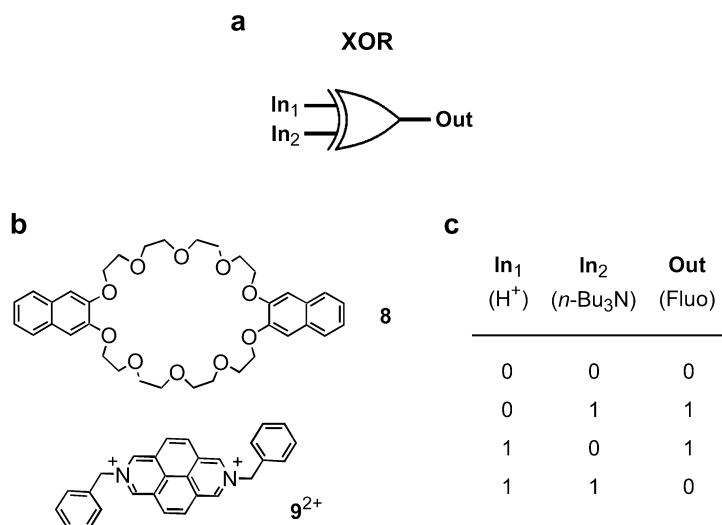


Fig. 7 Symbolic representation (a), molecular implementation (b), and truth table (c) of an XOR logic gate [24]. The working mechanism of the system is fully illustrated in Fig. 8.

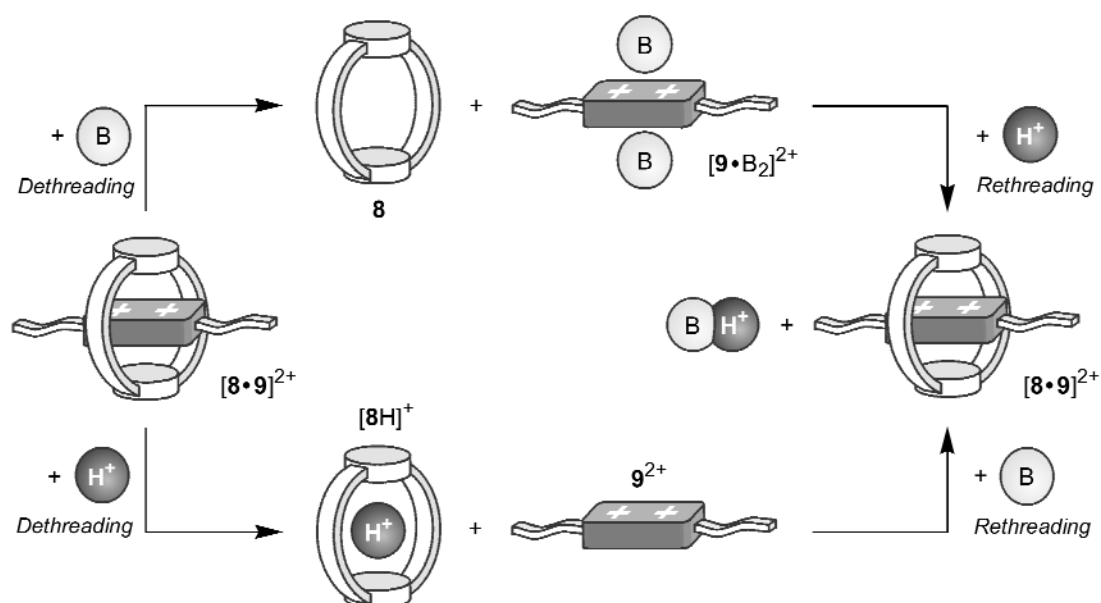


Fig. 8 Working mechanism of the XOR logic gate based on the compounds shown in Fig. 7b [24].

PHOTOCHEMICALLY DRIVEN MOLECULAR MACHINES

Dethreading/rethreading of pseudorotaxanes

Dethreading/rethreading of the wire and ring components of a pseudorotaxane reminds the movement of a piston in a cylinder. In order to achieve a light-induced dethreading in piston/cylinder systems, pseudorotaxanes have been designed which incorporate a “light-fueled” motor [26] (i.e., a photosensitizer) in the wire (Fig. 9a) [27] or in the macrocyclic ring (Fig. 9b) [28]. In both cases, in deaerated solution excitation of the photosensitizer with visible light in the presence of a sacrificial electron donor (e.g., triethanolamine) causes reduction of the electron-acceptor unit and, as a consequence, dethreading takes place. Rethreading can be obtained by allowing oxygen to enter the solution. It is worth noting that through a repeated sequence of deoxygenation and irradiation followed by oxygenation many dethreading/rethreading cycles can be performed on the same solution without any appreciable loss of signal until most of the reductant scavenger is consumed. As previously pointed out, however, photochemical systems which rely on such a sensitizer-scavenger strategy produce waste species from the decomposition of the reductant scavenger and from the consumption of dioxygen.

A system working on a completely different principle, in which dethreading/rethreading is exclusively governed by light energy without generation of any waste product, is illustrated in Fig. 10 [29]. The thread-like species *trans*-**10**, which contains a π -electron-rich azobiphenoxy unit, and the electron-accepting host **11**⁴⁺ self-assemble very efficiently ($K_{a,trans} = 1.5 \times 10^5 \text{ l mol}^{-1}$ in MeCN at 298 K) to give a pseudorotaxane. In the pseudorotaxane structure, the characteristic fluorescence of free **11**⁴⁺ is completely quenched by charge-transfer interactions. Irradiation with 365 nm light of a solution containing *trans*-**10** and **11**⁴⁺ ($1 \times 10^{-4} \text{ mol l}^{-1}$, 80 % complexed species) causes photoisomerization of *trans*-**10** to *cis*-**10**. Since the cyclophane interaction with *cis*-**10** ($K_{a,cis} = 1 \times 10^4 \text{ l mol}^{-1}$) is much weaker than that with *trans*-**10**, photoexcitation causes a dethreading process (Fig. 10), as indicated by the strong increase in the fluorescence intensity of **11**⁴⁺. On irradiation at 436 nm or by warming the solution in the dark the *trans* isomer can be reformed and, as a result, it rethreads inside the cyclophane.

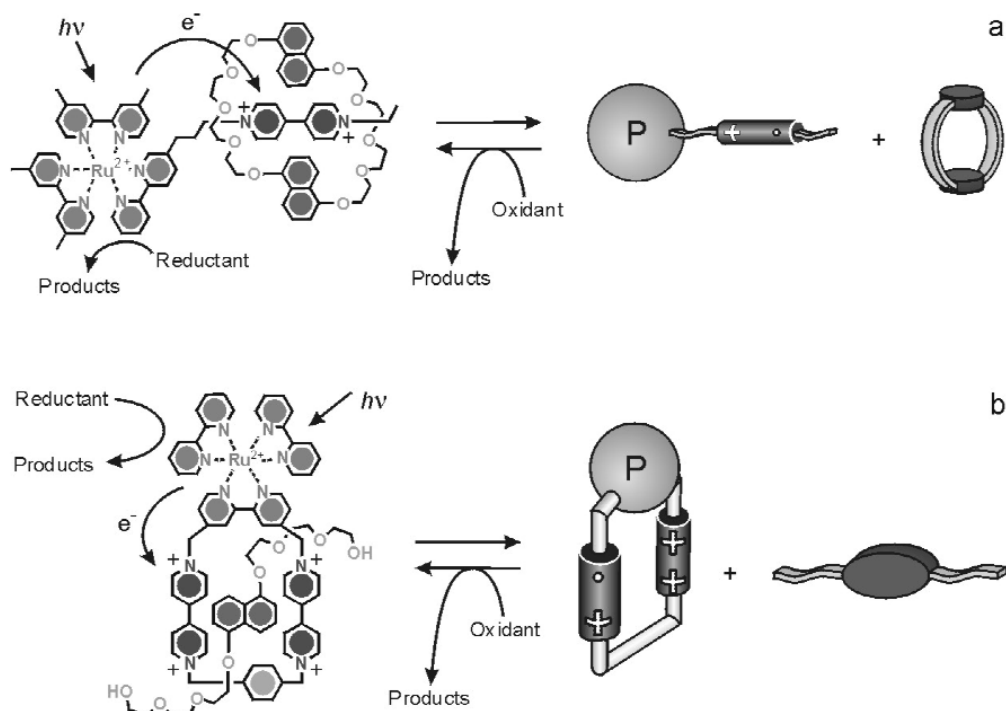


Fig. 9 Light-driven dethreading of pseudorotaxanes by excitation of a photosensitizer (a) contained in the wire-type component [27], and (b) incorporated in the macrocyclic ring [28].

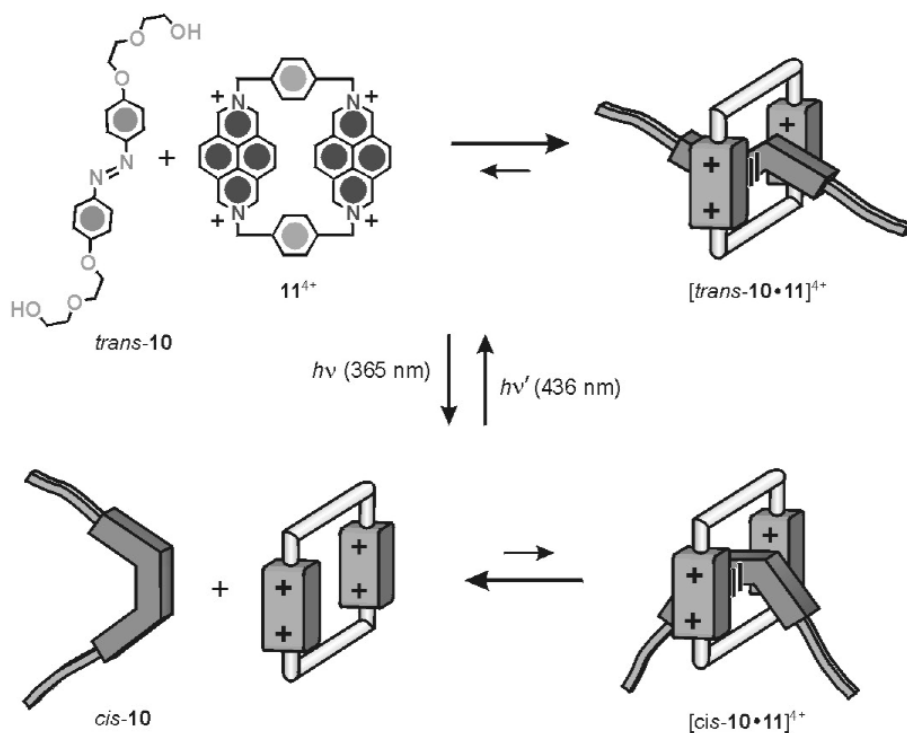


Fig. 10 Controllable dethreading/rethreading of a pseudorotaxane based on *trans-cis* photoisomerization [29].

A photocontrollable molecular shuttle

In order to achieve photoinduced ring switching in rotaxanes containing two different recognition sites in the dumbbell-shaped component, the thoroughly designed rotaxane shown in Fig. 11 was synthesized [30]. This compound is made of the electron-donor macrocycle **R**, and a dumbbell-shaped component which contains (i) $[\text{Ru}(\text{bpy})_3]^{2+}$ (**P**) as one of its stoppers, (ii) a 4,4'-bipyridinium unit (**A₁**) and a 3,3'-dimethyl-4,4'-bipyridinium unit (**A₂**) as electron-accepting stations, (iii) a *p*-terphenyl-type ring system as a rigid spacer (**S**), and (iv) a tetraarylmethane group as the second stopper (**T**). The structure of the rotaxane was characterized by mass spectrometry and NMR spectroscopy, which also established, along with cyclic voltammetry, that the stable translational isomer is the one in which the **R** component encircles the **A₁** unit, in keeping with the fact that this station is a better electron acceptor than the other one. The electrochemical, photophysical, and photochemical (under continuous and pulsed excitation) properties of the rotaxane, its dumbbell-shaped component, and some model compounds have then been investigated and two strategies have been devised in order to obtain the photoinduced abacus-like movement of the **R** macrocycle between the two stations **A₁** and **A₂**: one was fully based on processes involving only the rotaxane components (intramolecular mechanism), while the other one required the help of external reactants (sacrificial mechanism).

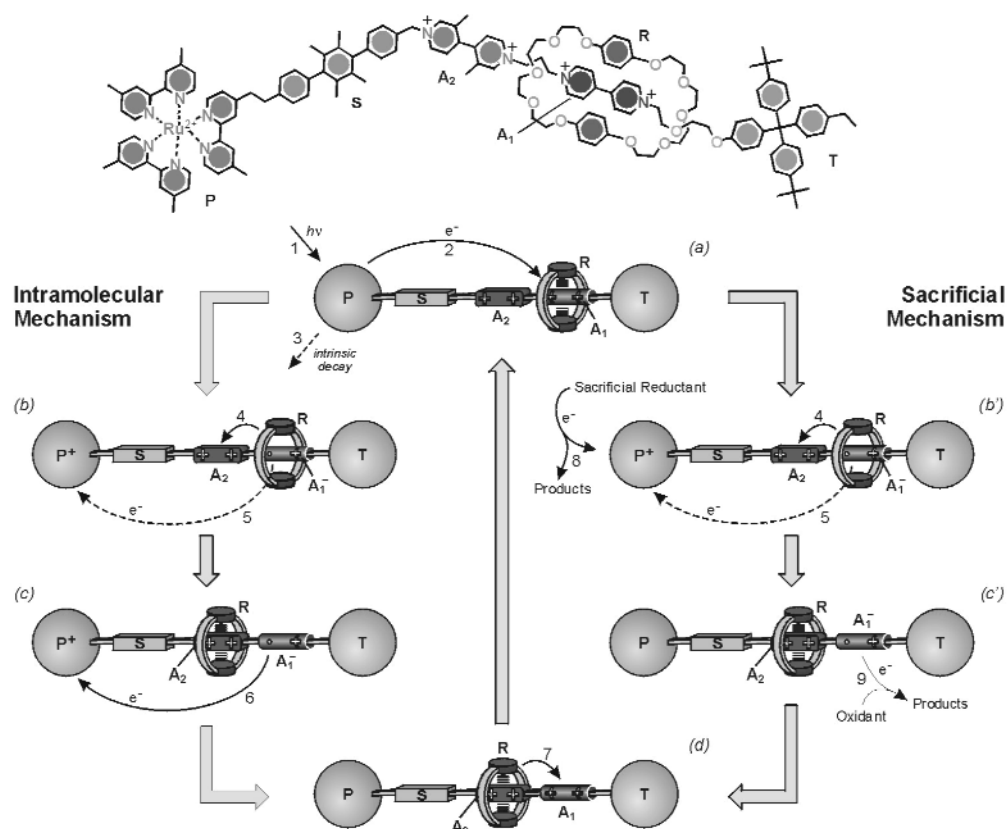


Fig. 11 Schematic representation of the intramolecular (left) and sacrificial (right) mechanisms for the photoinduced shuttling movement in a rotaxane [30].

The intramolecular mechanism, illustrated in the left-hand side of Fig. 11, is based on the following four operations [30]:

- (a) *Destabilization of the stable translational isomer*: light excitation of the photoactive unit **P** (Step 1) is followed by the transfer of an electron from the excited state to the **A₁** station, which is encircled by the ring **R** (Step 2), with the consequent “deactivation” of this station; such a photo-induced electron-transfer process has to compete with the intrinsic excited-state decay (Step 3).
- (b) *Ring displacement*: the ring moves from the reduced station **A₁⁻** to **A₂** (Step 4), a step that has to compete with the back electron-transfer process from **A₁⁻** (still encircled by **R**) to the oxidized photoactive unit **P⁺** (Step 5). This is the most difficult requirement to meet in the intramolecular mechanism.
- (c) *Electronic reset*: a back electron-transfer process from the “free” reduced station **A₁⁻** to **P⁺** (Step 6) restores the electron-acceptor power to the **A₁** station.
- (d) *Nuclear reset*: as a consequence of the electronic reset, back movement of the ring from **A₂** to **A₁** takes place (Step 7).

The results obtained seem to indicate that electronic reset of the system after light excitation (Step 5; $k = 2.4 \times 10^5 \text{ s}^{-1}$) is faster than the ring displacement (Step 4). We are now trying to modify the system in the attempt to further decrease the rate of the back electron-transfer reaction (Step 5) so as to achieve the displacement of the ring (Step 4) before the occurrence of electronic reset. It is worthwhile noticing that, in a system which behaves according to the intramolecular mechanism shown in the left-hand side part of Fig. 11, each light input causes the occurrence of a forward and back ring movement (i.e., a full cycle) without generation of any waste product. In some way, it can be considered as a “four-stroke” cyclic linear motor powered by light.

The alternative, less demanding sacrificial mechanism is based on the use of external redox reactants (a reductant-like triethanolamine, and an oxidant-like dioxygen) that operate as illustrated in right-hand part of Fig. 11 [30]:

- (a) Destabilization of the stable translational isomer, as in the previous mechanism.
- (b') Ring displacement after scavenging of the oxidized photoactive unit: since the solution contains a suitable reductant, a fast reaction of such species with **P⁺** (Step 8) competes successfully with the back electron-transfer reaction (Step 5); therefore, the originally occupied station remains in its reduced state **A₁⁻**, and the displacement of the ring **R** to **A₂** (Step 4), even if it is slow, does take place.
- (c') Electronic reset: after an appropriate time, restoration of the electron-acceptor power of the **A₁** station is obtained by oxidizing **A₁⁻** with a suitable oxidant such as dioxygen (Step 9).
- (d) Nuclear reset, as in the previous mechanism (Step 7).

The results obtained show that such a sacrificial mechanism is fully successful. Of course, this mechanism is less appealing than the intramolecular one because it causes the formation of waste products. Once again, it is worth noting that the mechanical movement of the macrocyclic component between the two stations and the related changes in the spectroscopic and electrochemical properties obey binary logic and can therefore be taken as a basis for information processing at the molecular level.

CONCLUSIONS

In his famous address to the American Physical Society, R. P. Feynman [31] concluded his reflection on the idea of constructing molecular-level machines as follows: “What would be the utility of such machines? Who knows? I cannot see exactly what would happen, but I can hardly doubt that when we have some control of the rearrangement of things on a molecular scale we will get an enormously greater range of possible properties that substances can have, and of different things we can do.” This sentence is still an appropriate comment to the work described in this paper, but now that several molecular-level

devices and machines have been designed and constructed, something more can be added. Two interesting kinds of applications of these systems begin to emerge: (i) their logic behavior can be exploited for information processing at the molecular level and, in the long run, for the construction of molecular-level (chemical) computers [14]; (ii) their mechanical features can be exploited for molecular-level transportation purposes, mechanical gating of molecular-level channels, and nanorobotics [32].

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